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CHEMICAL ENGINEERING DIVISION

THERMOCHEMICAL STUDIES

SEMIANNUAL REPORT

January-June 1971

W. N. Hubbard, P. A. G. O'Hare, G. K. Johnson,  
M. Ader, J. L. Settle, A. D. Tevebaugh,  
and R. C. Vogel



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July 1971





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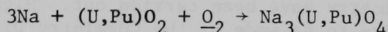
ABSTRACT

Preliminary values for enthalpies of formation have been determined as follows:  $\Delta H_f^{\circ}{}_{298}(\text{Na}_3\text{UO}_4, c) = \text{approx. } -480 \text{ kcal mol}^{-1}$ ;  $\Delta H_f^{\circ}{}_{298}(\text{Na}_2\text{O}, c) = -99.14 \pm 0.05 \text{ kcal mol}^{-1}$ ;  $\Delta H_f^{\circ}{}_{298}(\text{CsHC}_2, c) = +18.60 \pm 0.21 \text{ kcal mol}^{-1}$ ; and  $\Delta H_f^{\circ}{}_{298}(\text{XeF}_6, c) = -80.85 \pm 0.67 \text{ kcal mol}^{-1}$ . Exploratory studies have been started on ThS. A high-purity sample of technetium is being prepared for determinations of  $\Delta H_f^{\circ}(\text{TcF}_6)$  and  $\Delta H_f^{\circ}(\text{Tc}_2\text{O}_7)$ . The effect of  $\text{CO}_2$  in the HCl solution on the enthalpy of the HCl-tris(hydroxymethyl)aminomethane reaction has been studied. Quantum chemical investigations have been continued with calculations on the N-F, P-F, Cl-O, C-F, Si-F, and N-S systems.

SUMMARY

A Calorimetric Study of  $\text{Na}_3\text{UO}_4$

The failure of the fuel cladding in an oxide-fueled sodium-cooled reactor is postulated to lead to the reaction \*



A knowledge of the thermodynamic properties of the four species in the reaction enables one to calculate the oxygen pressure, one of the critical parameters of the process. In the above reaction, the oxygen, which is at a low level, originates in the fuel. It is believed that if the plutonium content of the fuel is ~20% or less, the enthalpy of formation of  $\text{Na}_3(\text{U,Pu})\text{O}_4$  ought to be very close to that of  $\text{Na}_3\text{UO}_4$ . For this reason, a sample of  $\text{Na}_3\text{UO}_4$  was prepared and characterized and its enthalpy of formation determined by enthalpy of solution measurements in an aqueous mixture of HCl and  $\text{XeO}_3$ .

Thermochemistry of  $\text{Na}_2\text{O}$

The enthalpy of formation of disodium oxide,  $\text{Na}_2\text{O}$ , is an important datum for use in the elucidation of the thermodynamics of the sodium-uranium-oxygen system, the importance of which was indicated above. The literature data for this quantity are discordant. A sample of  $\text{Na}_2\text{O}$  was purchased, heated under vacuum at  $510^\circ\text{C}$  for 40 hr to remove excess sodium

and any NaOH present, and used for enthalpy-of-solution measurements.

#### Enthalpy of Formation of $\text{CsHC}_2$

Values for the enthalpies of formation of the sodium acetylides  $\text{Na}_2\text{C}_2$  and  $\text{NaHC}_2$  were reported in the preceding annual report. They were determined because  $\text{Na}_2\text{C}_2$  has been postulated as playing an important role in the transport of carbon in sodium-cooled reactors. A similar study was planned for the cesium acetylides because the techniques for the measurements were available and because cesium is a high-yield fission product and dicesium acetylide might be formed in carbide fuel systems. Furthermore, literature data on fission-product carbides is so sparse that any addition is an aid in estimating nonexistent values. No sample of  $\text{Cs}_2\text{C}_2$  was available, but enthalpy-of-reaction measurements of  $\text{CsHC}_2$  with  $\text{CsOH}$  were made and combined with auxiliary thermochemical data to obtain the enthalpy of formation of  $\text{CsHC}_2$ .

#### Enthalpy of Formation of $\text{XeF}_6$

The determination of the enthalpy of formation of  $\text{XeF}_6$  crystal by reaction with  $\text{PF}_3$  gas has been concluded. The previous study of the enthalpy of fluorination of  $\text{PF}_3$  was checked as part of the investigation because of a recent publication reporting a discordant value.

#### Enthalpy of Formation of $\text{ThS}$

A cooperative study of the thermodynamic properties of thorium monosulfide is under way. A sample was prepared, and low temperature heat-capacity measurements were recently completed by H. E. Flotow and D. W. Osborne of the Chemistry Division. The sample is now available for room-temperature enthalpy-of-formation measurements in our group. Some preliminary measurements by both fluorine bomb calorimetry and solution calorimetry have been carried out. High-temperature vapor pressure studies were to be made by the Chemistry Division, but these studies have been delayed.

#### Enthalpies of Formation of $\text{TcF}_6$ and $\text{Tc}_2\text{O}_7$

A study of the enthalpies of formation of  $\text{TcF}_6(\text{g})$  and  $\text{Tc}_2\text{O}_7(\text{c})$  has been initiated. A sample of high-purity technetium metal is in preparation in the Materials Science Division.

#### Effect of $\text{CO}_2$ on the Enthalpy of Solution of Tris(hydroxymethyl)aminomethane

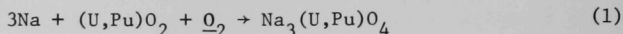
Tris(hydroxymethyl)aminomethane, TRIS, has been adopted as an enthalpy-of-solution standard. However, attempts by the National Bureau of Standards to certify its enthalpy of solution value have met with certain problems. This laboratory has been asked to study the problems. The first study was to investigate the effect of  $\text{CO}_2$  in the HCl solution on the enthalpy of the TRIS-HCl reaction.

## Quantum-chemical Investigations

Quantum-chemical investigations have continued with calculations on the nitrogen-fluorine, phosphorus-fluorine, chlorine-oxygen, carbon-fluorine, silicon-fluorine, and the nitrogen-sulfur systems.

I. A CALORIMETRIC STUDY OF TRISODIUM URANIUM(V) OXIDE,  $\text{Na}_3\text{UO}_4$   
(P. A. G. O'Hare)

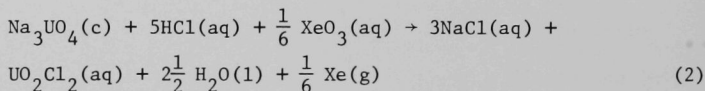
The failure of the fuel cladding in a oxide-fueled, sodium-cooled reactor and the consequent contact between sodium coolant and the fuel is postulated to lead to the following reaction:



One of the critical parameters of the above process is the oxygen pressure. In the above reaction, the oxygen, which is of a low level, originates in the fuel. A knowledge of the thermodynamic properties of the four species in reaction 1 enables one to calculate the oxygen pressure. However, to date, no significant thermodynamic data are available for  $\text{Na}_3(\text{U,Pu})\text{O}_4$ . On the basis of thermodynamic data for analogous uranium and plutonium systems (e.g., nitrides and oxides), it is assumed that at plutonium contents of 20% or less, the enthalpy of formation,  $\Delta H_f^\circ$ , of  $\text{Na}_3(\text{U,Pu})\text{O}_4$  is close to that of  $\text{Na}_3\text{UO}_4$ .

A specimen of  $\text{Na}_3\text{UO}_4$  was prepared (see ANL-7775, Section III.C) by the reaction of  $\text{Na}_2\text{O}$  with hyperstoichiometric  $\text{UO}_2$ . This specimen has been characterized by means of chemical, X-ray, and metallographic analyses.

The overall calorimetric reaction can be summarized as follows:



The calorimetric phase of the present study involved measurements of the heats of

- (a) the reaction between  $\text{Na}_3\text{UO}_4$  and an aqueous mixture of HCl and  $\text{XeO}_3$ ,
- (b) the solution of NaCl in HCl,
- (c) the solution of  $\text{UO}_2\text{Cl}_2$  in a mixture of NaCl and HCl, and
- (d) the solution of  $\text{XeO}_3$  in a mixture of NaCl, HCl, and  $\text{UO}_2\text{Cl}_2$ .

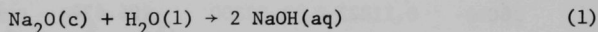
Combination of the measured heats with enthalpy-of-formation data from the literature indicate a preliminary value of about  $-480 \text{ kcal mol}^{-1}$  for  $\Delta H_f^\circ(\text{Na}_3\text{UO}_4)$ .

## II. THE THERMOCHEMISTRY OF DISODIUM OXIDE, $\text{Na}_2\text{O}$ (P. A. G. O'Hare)

As indicated in the previous annual report,<sup>1</sup> the determination of the enthalpy of formation of disodium oxide,  $\Delta H_{298}^\circ(\text{Na}_2\text{O})$ , is planned for two reasons: first, the values already in the literature for this compound are discordant; second,  $\Delta H_{298}^\circ(\text{Na}_2\text{O})$  is an important datum for use in the elucidation of the thermodynamics of the Na-U-O system.

A sample of disodium oxide obtained from Alfa Inorganics, Inc. was found to contain excess uncombined sodium. This material was heated under vacuum at  $510 \pm 10^\circ\text{C}$  for 40 hr. In this way, the excess sodium (several percent) was removed. It is also believed likely that any NaOH impurity was removed also. This conclusion is based on Hildenbrand and Murad's<sup>2</sup> mass-spectrometric observation that when a sample of  $\text{Na}_2\text{O}$  contaminated with NaOH was baked under vacuum for two days at about  $500^\circ\text{C}$ , all hydroxide was removed, as evidenced by the disappearance of  $\text{NaOH}^+$  and  $\text{Na}_2\text{OH}^+$  peaks in the mass spectrum. A small portion of our purified specimen was treated with aqueous hydrochloric acid; gas-chromatographic examination revealed no  $\text{CO}_2$ . Consequently, we believe that the material was essentially carbonate-free. Volumetric analysis indicated a purity of  $99.9 \pm 0.2\%$ .

Ten calorimetric measurements were performed for the reaction



The results are given in Table II-1. The headings of the table are as follows: the experiment number;  $m(\text{Na}_2\text{O})$ , the mass of  $\text{Na}_2\text{O}$  sample reacted;  $\Delta t_c$ , the temperature rise of the calorimeter corrected for heat exchange with the surroundings;  $\epsilon(\text{Calor.})$ , the energy equivalent of the calorimeter;  $\Delta H_{\text{vap}}$ , a small correction for saturation of the gas space of the ampoule, and  $\Delta H/M$ , the enthalpy of the reaction expressed as calories per gram of  $\text{Na}_2\text{O}$ . Experiment 4C was rejected because for some unknown reason the water-vapor level in the glovebox increased substantially while the sample for this run was being loaded.

Our measured heat of reaction is about  $1 \text{ kcal mol}^{-1}$  ( $\sim 15 \text{ cal g}^{-1}$ ) more exothermic than previous determinations (see Table II-2). It is believed that previous  $\text{Na}_2\text{O}$  preparations were contaminated with NaOH; this would cause the measured heats of reaction to be less exothermic than that measured by us.

<sup>1</sup> P. A. G. O'Hare, "Thermochemistry of  $\text{Na}_3\text{UO}_4$  and  $\text{Na}_2\text{O}$ " in Chemical Engineering Division Annual Report--1970, USAEC report ANL-7775 (in press).

<sup>2</sup> D. L. Hildenbrand and E. Murad, J. Chem. Phys. **53**, 3403 (1970).

TABLE II-1. Calorimetric Data for Sodium Oxide Experiments

Expt. No.	$\underline{m}(\text{Na}_2\text{O})$ (g)	$\Delta \underline{t}_c$ (deg C)	$\epsilon(\text{Calor.})$ (cal deg <sup>-1</sup> )	$\Delta \underline{H}_{\text{vap}}$ (cal)	$\Delta \underline{H}/\underline{M}$ (cal g <sup>-1</sup> )
1C	0.11829	1.02087	106.787	-0.013	-921.71
2C	0.11757	1.01340	106.762	-0.013	-920.35
3C	0.11834	1.02229	106.825	-0.013	-922.93
5C	0.11766	1.01733	106.787	-0.013	-923.43
6C	0.11244	0.97067	106.770	-0.013	-921.83
7C	0.11697	1.00997	106.600	-0.013	-920.54
8C	0.11822	1.02200	106.674	-0.013	-922.30
9C	0.11797	1.02150	106.643	-0.013	-923.53
10C	0.11586	1.00207	106.656	-0.013	-922.58
Mean $\Delta \underline{H}/\underline{M} = -922.13 \pm 0.38 \text{ cal g}^{-1}$					



TABLE II-2. Comparison of Previous Data for  $\Delta H_f^\circ(\text{Na}_2\text{O}, \text{c})$   
with This Work

Investigator	Reaction	$\Delta H_r$ (kcal mol <sup>-1</sup> )	$\Delta H_f^\circ(\text{Na}_2\text{O})_{298}$ (kcal mol <sup>-1</sup> )
Matsui (1929) <sup>3</sup>	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \cdot 1000\text{H}_2\text{O}$	$-56.53 \pm 0.16$	$-100.08 \pm 0.32$
Matsui (1929) <sup>4</sup>	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \cdot 1000\text{H}_2\text{O}$	$-56.64 \pm 0.07$	$-99.89 \pm 0.14$
Roth (1948) <sup>5</sup>	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \cdot 1000\text{H}_2\text{O}$	$-56.00 \pm 0.13$	$-100.60 \pm 0.26$
This work	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \cdot 1000\text{H}_2\text{O}$	$-57.22 \pm 0.05$	$-99.15 \pm 0.05$
Rengade (1907) <sup>6</sup>	$2\text{Na} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{O} + \text{H}_2$	-28.7	-97.02
de Forcrand (1900) <sup>7</sup>	$\text{Na}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$	-27.8	-94.90

<sup>3</sup> M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) **32**, 79 (1929).

<sup>4</sup> M. Matsui and S. Oka, Ibid. **32**, 83 (1929).

<sup>5</sup> W. A. Roth, Z. Anorg. Allg. Chem. **255**, 324 (1948).

<sup>6</sup> E. Rengade, Compt. rend. **145**, 236 (1907).

<sup>7</sup> de Forcrand, Compt. rend. **130**, 1465 (1900).

### III. THE ENTHALPY OF FORMATION OF MONOCESIUM ACETYLIDE, $\text{CsHC}_2$ (M. Ader)

Determination of the standard enthalpy of formation of monocationic acetylide,  $\Delta H_f^{\circ}{}_{98}(\text{CsHC}_2, \text{c})$ , was undertaken as a byproduct of our interest in fission-product carbides which, in turn, stems from the long-range potential of carbide-fueled fast breeder reactors. Dicationic acetylide,  $\text{Cs}_2\text{C}_2$ , was of particular interest: cesium is a high-yield fission product, and the anticipated instability of  $\text{Cs}_2\text{C}_2$  provides a mechanism for carbon transport and consequent deleterious effects, such as carburization of stainless steel cladding.

Initially, it was hoped that the enthalpies of formation of  $\text{CsHC}_2$  and  $\text{Cs}_2\text{C}_2$  could both be determined as had previously been done<sup>1</sup> for the analogous sodium compounds  $\text{NaHC}_2$  and  $\text{Na}_2\text{C}_2$ . However, the vendor<sup>2</sup> supplying us with these acetylides was unable to prepare  $\text{Cs}_2\text{C}_2$  by thermal decomposition of  $\text{CsHC}_2$ , the recommended method. The  $\text{CsHC}_2$  was synthesized by the reaction of liquid ammonia solutions containing cesium and acetylene and subsequent isolation of the product by evaporation of the solvent. Attempts by the vendor to convert  $\text{CsHC}_2$  to  $\text{Cs}_2\text{C}_2$  by vacuum heating, as had been done to convert  $\text{NaHC}_2$  to  $\text{Na}_2\text{C}_2$ , were unsuccessful. A brown, viscous, tacky decomposition product was obtained instead. (Moissan<sup>3</sup> in 1903 had reported that the decomposition of  $\text{CsHC}_2$  to  $\text{Cs}_2\text{C}_2$  was feasible at 300°C, but Corbellini and Turner<sup>4</sup> in 1960 could not confirm this reaction.) Thus, only the  $\text{CsHC}_2$  was received and investigated; the projected investigation of  $\text{Cs}_2\text{C}_2$  was dropped.

Calorimetric measurements of the enthalpy of reaction of  $\text{CsHC}_2$  with 0.018N  $\text{CsOH}$  were combined with auxiliary thermochemical data to obtain the enthalpy of formation of  $\text{CsHC}_2$  at 25°C. The experimental technique was essentially identical to that described in the preceding report.<sup>1</sup> In a helium-atmosphere glovebox (0.1-0.5 ppm  $\text{H}_2\text{O}$ ), the  $\text{CsHC}_2$  samples (0.55-0.56 g) were sealed into cylindrical Kel-F ampoules (0.375-in. OD by 0.300-in. ID by 9/16 in. long) having either 2- or 5-mil-thick end windows. The end windows were pierced while the ampoule was submerged and rotated in acetylene-saturated  $\text{CsOH}$  (~99 ml) which was contained in an LKB-8700 glass solution-and-reaction calorimeter modified for quartz-crystal thermometry.

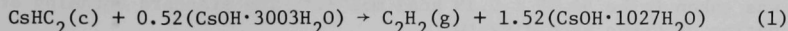
<sup>1</sup> G. K. Johnson and E. H. Van Deventer, "Enthalpies of Formation of Disodium and Monosodium Acetylides" in Chemical Engineering Division Annual Report--1970, USAEC report ANL-7775, in press.

<sup>2</sup> Alfa Inorganics, Inc., Beverly, Massachusetts.

<sup>3</sup> H. Moissan, C. R. Acad. Sci., Paris **136**, 1217 (1903).

<sup>4</sup> M. Corbellini and L. Turner, Chim. Ind. (Milan) **42**, 251 (1960).

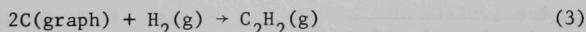
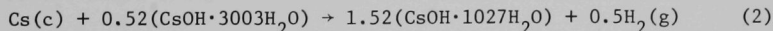
The enthalpies obtained for the reaction



fell into two sets:  $-82.95 \pm 0.26$  (1 $\sigma$ ) and  $-80.16 \pm 0.15$  (1 $\sigma$ ) cal g<sup>-1</sup>. No satisfactory reason for the discrepancy has been uncovered. The lower value is preferred because it comprises a larger number of measurements (9 versus 5), all but one of which were made after the measurements giving higher values, and therefore with the benefit of more experience and confidence in the experimental procedures.

Purity of the CsHC<sub>2</sub> was established by the following: (1) Metallic impurities were determined by emission spectrochemical and atomic absorption analyses. Less than 100 ppm total of lithium, sodium, potassium, and rubidium were found; other metals were present in much smaller amounts. Thus, thermal corrections for metallic contaminants could be ignored. (2) The cesium content was obtained indirectly by hydrolyzing CsHC<sub>2</sub> samples in isopropyl alcohol and titrating the hydrolysate with standard HCl. In the absence of other metals, the OH<sup>-</sup> found by this procedure is equivalent to cesium concentration. The average of three analyses was  $83.9 \pm 0.4\%$  Cs, or 99.7% of the theoretical cesium content of CsHC<sub>2</sub>. (3) Acetylide content was determined by hydrolyzing CsHC<sub>2</sub> and manometrically measuring the C<sub>2</sub>H<sub>2</sub>(g) evolved. Two such analyses showed 98.9 and 99.0% of the theoretical acetylide content of CsHC<sub>2</sub>. Gas chromatographic analysis of the gaseous product, even after acidification of the CsOH solution, indicated only a trace of CO<sub>2</sub>(g), or negligible carbonate contamination of the CsHC<sub>2</sub>. (4) Oxygen concentration in the CsHC<sub>2</sub> was found to be  $0.21 \pm 0.01\%$  by neutron activation analysis. The form of the oxygen is unknown, and the thermal correction for its presence represents the largest and most uncertain part of this investigation. CsOH and Cs<sub>2</sub>O are likely oxygen contaminants. If the oxygen impurity is CsOH, the estimated correction is  $+0.65$  cal g<sup>-1</sup> for the measured enthalpy of reaction of CsHC<sub>2</sub> with water; if oxygen is present as Cs<sub>2</sub>O, the estimated correction is  $+5.90$  cal g<sup>-1</sup>. In the calculations discussed below, the oxygen impurity is assumed to be CsOH(c).

The molar enthalpy of reaction 1, with all corrections applied, is  $\Delta H(1) = -12.66 \pm 0.08$  (2 $\sigma$ ) kcal mol<sup>-1</sup>. To derive the standard enthalpy of formation of CsHC<sub>2</sub> requires data for the following auxiliary reactions:

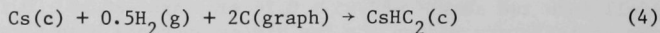


The enthalpy change for reaction 2 was obtained by combining Gunn's value<sup>5</sup> for the Cs(c)-H<sub>2</sub>O(l) reaction with heat-of-dilution data<sup>6</sup> for dilute NaOH solutions. (Negligible error is incurred by assuming that

<sup>5</sup> S. R. Gunn, *J. Phys. Chem.* **71**, 1386 (1967).

<sup>6</sup> V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2 (1965).

$\Delta H_{\text{dilution}}$  for NaOH and CsOH are similar.) The value obtained is  $\Delta H(2) = -48.25 \pm 0.01 \text{ kcal mol}^{-1}$ . The enthalpy of formation of  $\text{C}_2\text{H}_2(\text{g})$ ,  $\Delta H(3)$ , was taken to be  $54.19 \pm 0.19 \text{ kcal mol}^{-1}$ .<sup>7</sup> The standard enthalpy of formation of  $\text{CsHC}_2$  according to



is  $\Delta H_{298}^\circ(\text{CsHC}_2, \text{c}) = \Delta H(4) = -\Delta H(1) + \Delta H(2) + \Delta H(3) = 18.60 \pm 0.21 \text{ kcal mol}^{-1}$ .

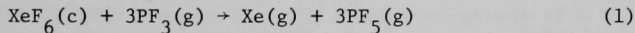
This result, when compared with the more positive value reported for  $\text{NaHC}_2$ <sup>1</sup> ( $\Delta H_{298}^\circ = 23.10 \pm 0.27 \text{ kcal mol}^{-1}$ ), indicates that  $\text{CsHC}_2$  is more stable. Dissimilar lattice structures as well as the difference in metal size may be responsible. The X-ray powder diffraction pattern of  $\text{CsHC}_2$  was found to be very complex and could not be identified. However, it did not originate from the  $\text{CaC}_2$ -type structure<sup>8</sup> characteristic of  $\text{NaHC}_2$ ,  $\text{KHC}_2$ , or  $\text{RbHC}_2$ .

<sup>7</sup> JANAF Thermochemical Tables, Dow Chemical Co., Midland, Michigan.

<sup>8</sup> H. Föppl, Angew. Chem. **70**, 401 (1958).

#### IV. THE ENTHALPY OF FORMATION OF XENON HEXAFLUORIDE, XeF<sub>6</sub> (G. K. Johnson)

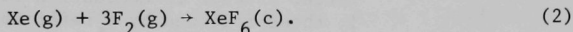
Since publication of the previous annual report (ANL-7775), a series of calorimetric reactions of crystalline xenon hexafluoride with gaseous phosphorus trifluoride according to



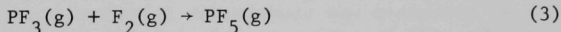
has been completed.

The combustions were carried out in a high-pressure two-chambered bomb with 15.3 atm of PF<sub>3</sub>(g) in the tank chamber. The mass of XeF<sub>6</sub> was determined by the difference in weight of a small cylinder containing XeF<sub>6</sub> before and after XeF<sub>6</sub> was charged into the bomb. The XeF<sub>6</sub> was distilled into the bomb through rigorously dried lines. The bomb was not opened or exposed to atmospheric moisture following the preconditioning experiments. Infrared analysis of the product gases showed only peaks for PF<sub>3</sub>, PF<sub>5</sub>, and a trace of POF<sub>3</sub>. The POF<sub>3</sub> is believed to have formed by hydrolysis of PF<sub>5</sub> with traces of water in the infrared cell.

The derived data for XeF<sub>6</sub>(c) are presented in Table IV-1. The combustion results refer to reaction 1 and the formation results to the reaction



The molecular weight of XeF<sub>6</sub> was taken to be 245.290 and the entropies,  $S_{298}^\circ$ , of F<sub>2</sub>(g), Xe(g), and XeF<sub>6</sub>(c) were taken to be 48.44,<sup>1</sup> 40.529,<sup>1</sup> and 50.282<sup>2</sup> cal K<sup>-1</sup> mol<sup>-1</sup>, respectively. The enthalpy of formation of XeF<sub>6</sub>(c) was calculated from  $\Delta H(1)$  and three times the enthalpy of fluorination of PF<sub>3</sub>, according to



which was previously measured at this Laboratory to be  $-151.99 \pm 0.16$  kcal mol<sup>-1</sup>.<sup>3</sup>

The enthalpy of formation of gaseous XeF<sub>6</sub> can be derived from the value for the solid using the enthalpy of sublimation of XeF<sub>6</sub>(c),

<sup>1</sup> D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, NBS Technical Note 270-3, U. S. Government Printing Office, Washington, D. C. (1968).

<sup>2</sup> F. Schreiner, D. W. Osborne, J. G. Malm, and G. N. McDonald, J. Chem. Phys. **51**, 4838 (1969).

<sup>3</sup> E. Rudzitis, E. H. Van Deventer, and W. N. Hubbard, J. Chem. Thermodyn. **2**, 221 (1970).

TABLE IV-1. Derived Results for  $\text{XeF}_6(\text{c})^{\text{a}}$

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$\Delta \text{Ec}^\circ / \text{M}$	=	$-1531.7 \pm 1.9 \text{ cal g}^{-1}$
$\Delta \text{Ec}^\circ$	=	$-375.71 \pm 0.47 \text{ kcal mol}^{-1}$
$\Delta \text{Hc}^\circ$	=	$-375.12 \pm 0.47 \text{ kcal mol}^{-1}$
$\Delta \text{Hf}^\circ$	=	$-80.85 \pm 0.67 \text{ kcal mol}^{-1}$
$\Delta \text{Sf}^\circ$	=	$-135.57 \text{ cal K}^{-1} \text{ mol}^{-1}$
$\Delta \text{Gf}^\circ$	=	$-40.43 \pm 0.67 \text{ kcal mol}^{-1}$

---

<sup>a</sup> Thermodynamic symbols followed by the letter c refer to combustion reaction 1; those followed by f refer to formation reaction 2; all data refer to 298.15K.

$\Delta H_{\text{sub}}^{\circ}(\text{XeF}_6, \text{c}) = 14,126 \pm 25 \text{ cal mol}^{-1}$ .<sup>4</sup> The result for  $\Delta H_f^{\circ}(\text{XeF}_6, \text{g})$  is  $-66.72 \pm 0.67 \text{ kcal mol}^{-1}$ .

In Table IV-2, the result for  $\text{XeF}_6(\text{g})$  obtained in this study is compared with several other available results. The agreement between the data from different sources is poor, with the data varying over a range of 26 kcal mol<sup>-1</sup>. Our data has been examined carefully for evidence of any systematic bias and none is evident. The data of Stein and Plurien<sup>5</sup> are preliminary results based on three combustions of a sample whose purity was estimated to be ~95%. Since their investigation has not been completed with a sample of better purity, their result is subject to much uncertainty. The data of Selph,<sup>6</sup> obtained by reaction with  $\text{PF}_3$ , is believed to be subject to a large systematic bias, as will be discussed below, and thus the result is of dubious value. The bomb calorimetric technique, when carefully employed, is generally a superior method for obtaining enthalpies of formation than are equilibrium or mass-spectrometric techniques. Thus the value reported herein for  $\Delta H_f^{\circ}(\text{XeF}_6, \text{g})$  is believed to be the best value available.

In addition to the  $\text{XeF}_6$  combustions reported above, a redetermination of the enthalpy of fluorination of  $\text{PF}_3$  (reaction 3) was undertaken. The latter study was conducted for two reasons. First, the data previously obtained at this Laboratory for  $\Delta H(3)$ ,  $-151.99 \pm 0.16 \text{ kcal mol}^{-1}$ ,<sup>3</sup> became subject to some question when Selph<sup>6</sup> subsequently studied the same reaction and obtained a value for  $\Delta H(3)$  of  $-131.1 \pm 0.7 \text{ kcal mol}^{-1}$ ; and second, the fluorine stripping properties of  $\text{PF}_3$  make it a generally useful calorimetric reactant for studying higher fluorides. Therefore, an accurate and precise value for  $\Delta H(3)$  is imperative.

The redetermination of the enthalpy of reaction of  $\text{PF}_3$  was done in two parts. First, a series of experiments was conducted in which a weighed amount of  $\text{PF}_3$  was reacted with an excess of  $\text{F}_2$ . This method was similar to that previously employed<sup>3</sup> and yielded a result for  $\Delta H(3)$  of  $-151.91 \pm 0.10 \text{ kcal mol}^{-1}$ , in excellent agreement with our previous result. Secondly, a series of experiments was conducted in which a weighed amount of  $\text{F}_2$  was reacted with an excess of  $\text{PF}_3$ . These latter conditions better duplicate the conditions that exist when  $\text{PF}_3$  is used as a fluorine stripper. In this case, the results show some variation, which can be correlated against the composition of the product gas as is discussed below. When the mole fraction of  $\text{PF}_5(\text{X}_{\text{PF}_5})$  in the  $\text{PF}_3$ - $\text{PF}_5$  product gas is greater than 0.5, the results show no variation with mole fraction  $\text{PF}_5$  and yield a value for  $\Delta H(3)$  of  $-151.97 \pm 0.10 \text{ kcal mol}^{-1}$ . This result is in good agreement with the data obtained in excess fluorine.

<sup>4</sup> F. Schreiner, Chemistry Division, ANL, unpublished results (1971).

<sup>5</sup> L. Stein and P. L. Plurien in Noble Gas Compounds, H. H. Hyman, Ed., p. 144, Univ. of Chicago Press (1963).

<sup>6</sup> C. C. Selph, thesis, Georgia Inst. of Technology (1970).



TABLE IV-2. Comparison of Previous Data for  $\Delta H_f^\circ(\text{XeF}_6, \text{g})$  with This Work

$\Delta H_f^\circ(\text{XeF}_6, \text{g})$	Method	Reference
-85.6 <sup>a</sup>	Combustion in $\text{H}_2$	5
-70.4	Equilibrium	7
-71.2 $\pm$ 1.8	Combustion in $\text{PF}_3$	6
-(92) <sup>+8</sup> <sub>-3</sub>	Photoionization-mass spectrometric	8
-66.72 $\pm$ 0.67	Combustion in $\text{PF}_3$	this work

<sup>a</sup> Reported value of -79 kcal mol<sup>-1</sup> revised by use of  $\Delta H_f^\circ(\text{HF}, \text{g}) = -65.35$  kcal mol<sup>-1</sup> rather than -64.2 kcal mol<sup>-1</sup> used by the author.

<sup>7</sup> B. Weinstock, E. E. Weaver, and C. P. Knop, Inorg. Chem. **5**, 2189 (1966).

<sup>8</sup> J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Spohr, Physics Division, ANL, unpublished results (1971).



However, when the mole fraction of  $\text{PF}_5$  in the product gas is less than 0.5,  $\Delta H(3)$  becomes more positive with decreasing  $X_{\text{PF}_5}$ . When the mole fraction of  $\text{PF}_5$  in the product gas is 0.25, the value for  $\Delta H(3)$  becomes  $-151.42 \pm 0.20 \text{ kcal mol}^{-1}$ , or  $0.55 \text{ kcal mol}^{-1}$  more positive. At this point, it is not evident why  $\Delta H(3)$  varies with mole fraction of  $\text{PF}_5$  when this quantity becomes smaller than 0.5. However, the data obtained in experiments with excess  $\text{F}_2$  agreed with the data obtained with excess  $\text{PF}_3$  and  $X_{\text{PF}_5}$  greater than 0.5. This is believed to be more than fortuitous. We consider our values for the enthalpy of fluorination of  $\text{PF}_3$  to be correct. The reactions are significantly different, and it is not likely that the same result would be obtained unless that result were correct. However, when  $\text{PF}_3$  is used as a fluorine stripper, it is important that  $X_{\text{PF}_5}$  in the product gas be greater than 0.5, or that the effect of mole fraction  $\text{PF}_5$  be determined. In the reaction of  $\text{XeF}_6$  with  $\text{PF}_3$  discussed above,  $X_{\text{PF}_5}$  in the product was greater than 0.5 and the data did not show any variation with sample or  $X_{\text{PF}_5}$ . The results obtained here for the enthalpy of fluorination of  $\text{PF}_3$  are inconsistent with the data of Selph. Apparently, his work has a large positive bias, both in the combustions of  $\text{XeF}_6$  ( $\sim 63 \text{ kcal mol}^{-1}$ ) and in the combustion of  $\text{PF}_3$  ( $\sim 21 \text{ kcal mol}^{-1}$ ). In deriving  $\Delta H_f^\circ(\text{XeF}_6, \text{g})$ , his biases are largely self-cancelling. However, the derived result must be considered highly questionable due to the magnitude of the bias.

V. THE ENTHALPY OF FORMATION OF THORIUM MONOSULFIDE, ThS  
(M. Ader)

Plans for a cooperative study of the thermodynamic properties of thorium monosulfide were made some time ago with the Chemistry Division. The sample was to be prepared and high-temperature vapor pressure studies were to be carried out by the Chemistry Division. Low-temperature heat-capacity measurements were to be made by H. E. Flotow and D. W. Osborne of the Chemistry Division and room-temperature enthalpy-of-formation measurements in our group. The sample was prepared, and the low-temperature heat-capacity studies were recently completed. The sample is now available for our study. The high-temperature vapor pressure studies to be undertaken by the Chemistry Division, however, have been delayed. We have made preliminary experiments without calorimetric measurement with "crude" ThS to find a suitable calorimetric technique. Two types of reactions were tried: (1) reaction with hydrochloric acid and (2) combustion in fluorine.

Acidic dissolution of ThS was suggested by the work of Eyring and Westrum,<sup>1</sup> who determined the enthalpy of formation of Th<sub>2</sub>S<sub>3</sub> by measuring its heat of solution in 6M HCl or 6M HCl-0.005M Na<sub>2</sub>SiF<sub>6</sub>. Accordingly, ~200 ml of each of these solvents was reacted at ~20°C with a sample of ThS weighing ~0.3 g. Dissolution accompanied by gas evolution occurred during 20 to 25 min; a residue remained in each solvent. The reaction is believed to be ThS(c) + 4HCl(aq) → ThCl<sub>4</sub>(aq) + H<sub>2</sub>S(g) + H<sub>2</sub>(g). Both residues weighed ~11% of the sample weight and were found by X-ray powder diffraction analyses to consist of equal amounts of ThS and ThOS. This result is not unexpected, since ThOS is insoluble in 6M HCl and since a minor amount of ThOS was identified in the ThS. Presumably, the fraction of insolubles would be reduced considerably by working with purer ThS.

Experimental combustions of ThS in fluorine were performed which if complete would be represented by the equation ThS(c) + 5F<sub>2</sub>(g) → ThF<sub>4</sub>(c) + SF<sub>6</sub>(g). Large granules or chunks of ThS did not ignite or change weight significantly when exposed to 1-4 atm of fluorine for 45 min. This indicated the need of a combustion aid or ignitor to initiate combustion. Powdered sulfur, which ignites spontaneously in fluorine, was tried at low fluorine pressures in a glass bomb so that the combustion could be observed. Experiments with fluorine pressures between 15 and 20 atm were conducted in a one-chambered nickel bomb, using electrical ignition of molybdenum fuse wire, molybdenum wire-molybdenum foil, or α-SiC to initiate the reaction. Generally, the product consisted of a button of fused ThF<sub>4</sub>, sublimed ThF<sub>4</sub> powder, and unreacted ThS. In all cases, whether the ThS sample was granular or fine, combustion was incomplete, but the combustion yield was improved with fine particles. Fine ThS sometimes ignited prematurely, indicating that a two-chambered bomb would

<sup>1</sup> L. Eyring and E. F. Westrum, Jr., *J. Amer. Chem. Soc.* **75**, 4802 (1953).

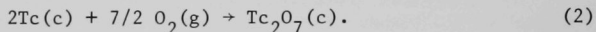
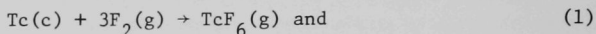
be required for calorimetric measurements. Tests in which nickel,  $\text{Al}_2\text{O}_3$ , and SiC were used as sample supports showed nickel to be superior. However, massive nickel supports seemed to quench the ThS reaction, whereas very thin nickel was itself consumed.

It appears from the results of these preliminary experiments that acidic dissolution and fluorine combustion are both feasible methods for determining the enthalpy of formation of ThS. Future efforts will be directed toward making calorimetric measurements and analyzing the products of reaction.

VI. THE ENTHALPIES OF FORMATION OF  $\text{TcF}_6$  and  $\text{Tc}_2\text{O}_7$   
(G. K. Johnson)

A study of the thermodynamic properties of  $\text{TcF}_6(\text{g})$  and  $\text{Tc}_2\text{O}_7(\text{c})$  has been initiated. Technetium is a significant fission product, and elucidation of the thermodynamic properties of the key compounds (fluoride and oxide) should be helpful in predicting the interactions of technetium compounds in reactor technology.

The enthalpies of formation of  $\text{TcF}_6(\text{g})$  and  $\text{Tc}_2\text{O}_7(\text{c})$  will be obtained by direct combination of the elements in a bomb calorimeter according to



These experiments will be conducted in the equipment which has been set up for studying plutonium compounds.

A sample of high-purity technetium metal is being prepared by G. W. Kosterz of the Materials Science Division. The calorimetric experiments will be performed on a portion of this sample.

VII. CALORIMETRIC STANDARDS: THE EFFECT OF CO<sub>2</sub> ON THE ENTHALPY OF SOLUTION OF TRIS(HYDROXYMETHYL)AMINOMETHANE IN HCl  
(G. K. Johnson, W. N. Hubbard)

The use of tris(hydroxymethyl)aminomethane or TRIS for an enthalpy-of-solution standard was proposed by Wadsö and Irving<sup>1</sup> at a meeting of the Task Group on Reference and Calibration Standards of the IUPAC Commission on Thermodynamics and Thermochemistry (July 23, 1963; Lund, Sweden). At this meeting, various reactions, including the TRIS-HCl reaction, were proposed as possible reference standards for solution calorimetry, and steps were taken to start a cooperative test program on the relative merits of the alternative proposals.

Following discussions at the Calorimetry Conference the same year, a number of laboratories made preliminary measurements on the TRIS-HCl reaction. The results were promising, and the following year (1964), the Calorimetry Conference voted to request the U. S. National Bureau of Standards to prepare a large, uniform batch of TRIS as a standard reference material, i.e., an enthalpy-of-solution standard. The Bureau accepted this request. A 6-kg batch was prepared and distributed to a selected group of laboratories, including this one, for a cooperative test program.

The program was a success except for the disturbing fact that the Bureau of Standards' own result was between 0.1 and 0.2% more exothermic than the results of many of the other laboratories. Consequently, the Bureau has delayed certification of the sample as a "standard sample". At the Calorimetry Conference last year, some preliminary data were presented by the Bureau that were interpreted to mean that saturation with CO<sub>2</sub> of the HCl solution used to dissolve TRIS leads to a value for the enthalpy of solution of TRIS almost 1% too exothermic. No reasonable explanation for this could be suggested by anyone.

Our laboratory has been asked by the Bureau to help in the solution of this problem. The first step has been to investigate the effect of CO<sub>2</sub> on the enthalpy of the TRIS-HCl reaction. A series of thirteen enthalpy-of-solution measurements has been completed. Both the original NBS test sample and the sample being prepared for certification were used. Both air-saturated and CO<sub>2</sub>-saturated 0.10N HCl solutions were used to dissolve the samples.

The results of the measurements are presented in Table VII-1. The items of the table are as follows: the experiment number; the gas with which the HCl was saturated and which was passed over the solution during the experiment; the mass in grams of TRIS dissolved;  $\Delta t_c$ , the temperature rise in degrees centigrade of the calorimeter corrected for heat exchange with the surroundings;  $\epsilon(\text{Calor.})$   $\Delta t_c$ , the total heat in calories evolved

<sup>1</sup> I. Wadsö and R. J. Irving, Acta Chem. Scand. **18**, 195 (1964).

TABLE VII-1. Enthalpy of Solution of TRIS in 0.10N HCl

Expt. No.	1	2	3	4	5	6	7	8 <sup>a</sup>	9 <sup>a</sup>	10 <sup>a</sup>	11	12	13
Gas	Air	CO <sub>2</sub>	Air	CO <sub>2</sub>	Air	CO <sub>2</sub>	Air	Air	CO <sub>2</sub>	Air	CO <sub>2</sub>	Air	Air
Mass TRIS, g	0.51743	0.51183	0.49664	0.50372	0.49816	0.50204	0.50068	0.49916	0.50030	0.49936	0.49799	0.49651	0.50153
$\Delta t_c$ , deg	0.28557	0.28112	0.27384	0.27600	0.27233	0.27592	0.27553	0.27499	0.27455	0.27503	0.27267	0.27363	0.27626
$\epsilon(\text{Calor.})\Delta t_c$ , cal	-30.430	-29.951	-29.156	-29.434	-28.999	-29.449	-29.353	-29.292	-29.269	-29.291	-29.072	-29.152	-29.426
$\Delta H_{\text{vap}}$ , cal	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004	-0.004
$n\Delta H_r$ , cal	-30.434	-29.955	-29.160	-29.438	-29.003	-29.453	-29.357	-29.296	-29.273	-29.295	-29.076	-29.156	-29.430
$\Delta H_r/M$ , cal/g	-58.818	-58.525	-58.715	-58.441	-58.220	-58.667	-58.634	-58.691	-58.511	-58.665	-58.387	-58.722	-58.680
$\Delta H_r$ , cal/mol	-7125.0	-7089.6	-7112.6	-7079.4	-7052.6	-7106.8	-7102.8	-7109.7	-7087.9	-7106.5	-7072.8	-7113.4	-7108.3

<sup>a</sup> Original NBS test samples of TRIS. In other experiments, samples of material being prepared for certification were used.

in the experiment;  $\Delta H_{\text{vap}}$ , the correction in calories for the vaporization of a small amount of  $\text{H}_2\text{O}$  to saturate the ampoule space; and the final three items are the heat in calories evolved by the reaction, expressed in calories per experiment, per gram, and per mole, respectively.

While several of the results obtained might be considered anomalous, the obvious conclusion is that the so-called effect of  $\text{CO}_2$  on the enthalpy-of-solution measurements observed by the Bureau is not even of the correct sign. For example, if experiments number 1, 5, and 6 are disregarded arbitrarily, the average values and standard deviations are  $-7108.9 \pm 1.6 \text{ cal mol}^{-1}$  for the experiments with air-saturated  $\text{HCl}$  and  $-7082.4 \pm 3.9 \text{ cal mol}^{-1}$  for the experiments with  $\text{CO}_2$ -saturated  $\text{HCl}$ .



VIII. QUANTUM-CHEMICAL INVESTIGATIONS OF SELECTED  
DIATOMIC MOLECULES AND IONS  
(P. A. G. O'Hare\*)

Since the last annual report (ANL-7775), our quantum-chemical studies have continued but at a substantially reduced rate. Significant data have been obtained for the bond energies, ionization potentials, and electron affinities of a variety of systems. In addition, a large number of one-electron properties, notably the dipole and quadrupole moments, have been calculated. A portion of the research has been described at scientific meetings<sup>1,2</sup> or is in the process of being published. An outline of the work performed during the past year follows:

A. The Nitrogen-Fluorine and the Phosphorus-Fluorine Systems

This phase of the investigation has been described in a recent publication,<sup>3</sup> the abstract of which is as follows:

A quantum chemical investigation of the nitrogen-fluorine and phosphorus-fluorine diatomic systems is described. Molecular self-consistent-field wavefunctions near the Hartree-Fock limit were computed via the Roothaan expansion method for the  $X^3\Sigma^-$  (ground),  $a^1\Delta$ , and  $b^1\Sigma^+$  states of NF and for the  $2\Pi$  states of  $NF^+$  and  $NF^-$ . Similar wavefunctions were computed for the  $3\Sigma^-$  ground state of PF and for  $PF^+(2\Pi)$ . For the neutral molecules, the experimental bond lengths were used; for the charged species, the internuclear separations of the parent ( $3\Sigma^-$ ) molecules were used. In addition, a wavefunction was obtained for  $PF^+(2\Pi)$  at its experimental internuclear separation. Values derived for the binding and ionization energies through the use of semiempirical correlation energies are in excellent agreement with experimental data; the uncorrelated excitation energies, as expected, are somewhat different than the experimental results. The electron affinities deduced from the wavefunctions indicate that the hitherto unreported  $NF^-$  and  $PF^-$  should be thermodynamically stable at moderate temperatures. Dipole and quadrupole moments have also been calculated for all the species. The second ionization potential of PF has been estimated based on Koopmans' theorem.

\* This work was performed in collaboration with A. C. Wahl, Chemistry Division.

<sup>1</sup> P. A. G. O'Hare and A. C. Wahl, "A Quantum Chemical Study of SF and PF," 3rd European Symposium on Fluorine Chemistry, Aix-en-Provence, France, September 1970.

<sup>2</sup> P. A. G. O'Hare, Amer. Chem. Soc. 161st National Meeting, Los Angeles, Calif., March 1966. Abstracts of Papers, No. PHYS-087.

<sup>3</sup> P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys., in press.



B. The Chlorine-Oxygen System

This system was of interest to us because it is isoelectronic with the SF system, which formed the subject matter of a previous publication.<sup>4</sup> A paper<sup>5</sup> describing our investigation of the Cl-O system is now in press. The abstract of that paper is as follows:

Molecular self-consistent-field wave functions near the Hartree-Fock limit have been computed by the Roothaan expansion method for  $\text{ClO}(\text{}^2\Pi)$ ,  $\text{ClO}^+(\text{}^3\Sigma)$ , and  $\text{ClO}^-(\text{}^1\Sigma)$  at an internuclear separation of 1.570 Å. Combination of the computed total energies with estimates for the molecular extra correlation energies yielded values of  $<2.9$ ,  $2.2 \pm 0.5$ , and  $11.2 \pm 0.4$  eV for the binding energy, vertical electron affinity, and vertical ionization potential, respectively, of ClO. The above results, and the computed dipole moment,  $0.81 \pm 0.16$  D, are in satisfactory agreement with experimental data. In addition to the above properties, the dipole and quadrupole moments have been calculated for  $\text{ClO}^+$  and  $\text{ClO}^-$ .

C. The Carbon-Fluorine and Silicon-Fluorine Systems

Our most recent study on fluoride systems involved the CF and SiF molecules. This investigation is described in a publication,<sup>6</sup> the abstract of which is as follows:

Accurate Hartree-Fock self-consistent-field wavefunctions have been computed for CF,  $\text{CF}^+$ , and  $\text{CF}^-$  at several internuclear separations by the Roothaan expansion method. Similar wavefunctions were also computed for SiF,  $\text{SiF}^+$ , and  $\text{SiF}^-$  at the parent molecule internuclear separation. A Dunham analysis of the energy curves for the three CF species yielded values for the spectroscopic constants. Other properties deduced in the present research include the first and second ionization potentials, electron affinities, and dipole and quadrupole moments for CF and SiF. The dipole moment calculated for CF is consistent with a charge distribution corresponding to a  $\text{C}^--\text{F}^+$  configuration. In addition, the correlation energies of a number of light-element diatomic fluorides have been deduced from literature data and from results given in the present paper. It appears that the correlation energy increment between adjacent diatomic fluorides is virtually constant for molecules of the first row of the periodic table.

<sup>4</sup>P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. **53**, 2834 (1970).

<sup>5</sup>P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. **54**, 3770 (1971).

<sup>6</sup>P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys., in press.

Further results from the above study, including the complete wavefunctions and the charge-density diagrams, have been given in a report.<sup>7</sup> The abstract of this report is as follows:

Complete Hartree-Fock wavefunctions, calculated by the open-shell method of Roothaan, are given for  $\text{CF}(^2\Pi)$ ,  $\text{CF}^+(^1\Sigma)$ , and  $\text{CF}^-(^3\Sigma)$  at several internuclear separations. Expectation values for selected operators are tabulated. Charge-density diagrams for  $\text{CF}(^2\Pi)$  and each of its component orbitals are also included in the report.

#### D. The Nitrogen-Sulfur System

We recently described<sup>8</sup> a molecular orbital study of NS and  $\text{NS}^+$ . The results from this study were in excellent agreement with various experimental data obtained by ourselves and other investigators. More recently, we have computed an accurate wavefunction for  $\text{NS}^-(^3\Sigma)$  and have deduced  $1.3 \pm 0.3$  eV for the electron affinity of NS. To date, this value has not been determined experimentally.

The research on  $\text{NS}^-$  is described in a note,<sup>9</sup> which has been accepted for publication.

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<sup>7</sup> P. A. G. O'Hare and A. C. Wahl, Complete Hartree-Fock Wavefunctions and One-Electron Properties for  $\text{CF}(^2\Pi)$ ,  $\text{CF}^+(^1\Sigma)$  and  $\text{CF}^-(^3\Sigma)$ , and Charge Density Diagrams for CF and its Component Orbitals, USAEC Report ANL-7806, in press.

<sup>8</sup> P. A. G. O'Hare, J. Chem. Phys. 52, 2992 (1970).

<sup>9</sup> P. A. G. O'Hare, J. Chem. Phys. 54, 4124 (1971).

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